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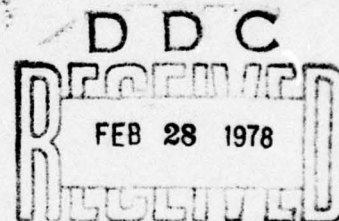
**TORSIONAL PENDULUM STUDY ON
SEVERAL EPOXY/DIAMINE POLYMERS**

BY G. F. LEE

RESEARCH AND TECHNOLOGY DEPARTMENT

31 OCTOBER 1977

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strongly influenced by the degree of aromaticity and chain length of the amine monomers. The activation energies of the gamma transition were between 17 and 29 kcal/mole. The gamma transition, which occurs at -55°C at 1 Hz, dominated the ultrasonic properties of these polymers around room temperature.

The torsional pendulum was shown to be a convenient method to determine the ultrasonic properties of polymers provided the activation energies of the gamma transition are known.

SUMMARY

This report describes work done on several epoxy/diamine polymers. The goal of this work was to determine the shear properties as a function of temperature by utilizing a low frequency (~ 1 Hz) torsional pendulum. Then applying the Arrhenius shift the data was shifted to a frequency of 1.8 MHz as a function of temperature. From this data, the shear sound speed and absorption were calculated.

This work was carried out during FY 77 with funds provided by the NSWC Internal Research Project on Polymer Impact Resistance (IR-738).

J. R. Dixon
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INTRODUCTION

Knowledge of structure to property relations in polymers is valuable since this information can be used to predict the properties of any given new polymer and also to guide the synthesis of polymers with tailor made properties for specific engineering applications. Many studies¹⁻⁷ have been done on the epoxy-amine polymers of 2,2-bis p-(2,3-epoxypropoxy) phenyl -propane, commonly known as diglycidyl ether of bisphenol A (DGEBA), with 1,3-Propanediamine (PDA), 1,6-Hexanediamine (HDA), 1,12-Dodecanediamine (DDA), and m-Phenylenediamine (MPDA). There are relatively few reports in the scientific literature concerning torsional pendulum properties, glass and secondary transition temperatures on the polymers of m-bis(2,3-epoxypropoxy)-benzene or resorcinol diglycidyl ether (RDGE) and 1,4-bis(2,3-epoxypropoxy)-butane or butanediol diglycidyl ether (BDGE) with the above diamines.

The purpose of the study is to determine the thermomechanical properties of the following epoxies: DGEBA, RDGE, and BDGE cured with the following diamines: PDA, HDA, DDA, and MPDA. Also the activation energy of the sub-glass transition (γ) will be determined and whenever possible the structure to property relationship will be made. Using the above activation energy, the shear sound speed and absorption will be determined at 1.8 MHz. This frequency was chosen because apparatus for making measurements at this frequency is available.

EXPERIMENTAL

Materials - The preparation and physical properties of the epoxy and diamine monomers have already been reported.⁸ The structures of these monomers are listed in Table 1.

1. Krehling, R. P., and Kline, D. E., J. Appl. Polym. Sci., 13, 2411 (1969).
2. Murayama, T., and Bell, J. P., J. Polym. Sci., A-2, 8, 437 (1970).
3. Bell, J. P., J. Polym. Sci., A-2, 6, 417 (1970).
4. Pogany, G. A., Polym., 11, 66 (1970).
5. Delatycki, O., Shaw, J. C., and Williams, J. G., J. Polym. Sci., A-2, 7, 753 (1969).
6. Kline, D. E., J. Polym. Sci., XLVII, 237 (1960).
7. Pogany, G. A., Eur. Polym. J., 6, 343 (1970).
8. Booth, H. J., NOLTR 73-112, July (1973).

Torsional Pendulum Measurements - The torsional pendulum (TP) was built from the designs of Nielsen.⁹ This apparatus is a convenient method to determine transitions in polymers.

The purpose of the torsional pendulum is to excite the test sample in free oscillation at 1 Hz. These oscillations are recorded on a strip-chart recorder as damped sine waves. From the damped sine waves two mechanical properties are obtained, shear modulus and logarithmic decrement determined as a function of temperature. The temperature range was from -175 to 200°C. The shear modulus (G) was calculated using the expression:

$$G = \frac{2.35 L I}{C D^3 \mu P^2} \text{ (dynes/cm}^2\text{)} \quad (1)$$

where L is the length of the sample between the clamps in cm, C is the width of the sample in cm, D is the thickness of the sample in cm, I is the moment of inertia of the oscillating system in g-cm², μ is the shape factor, and P is the period of oscillations in seconds. The logarithmic decrement (Δ) was calculated from the relationship

$$\Delta = \frac{1}{n} \ln \frac{A(r)}{A(r+n)} \quad (2)$$

where A(r) is the reference peak amplitude and A(r+n) is the peak amplitude n cycles later.

The test sample size was approximately 7.87 x 1.02 x 0.23 cm.

Activation Energy - The activation energy (H) was determined by calculating the area under the loss factor versus reciprocal temperature curve.¹⁰ The activation energy was calculated from the expression

$$\left\langle \frac{1}{H} \right\rangle_{av}^{-1} = \frac{R \pi (G_U - G_R)}{2 \int_0^\infty G'' d(1/T)} \text{ (cal/mol)} \quad (3)$$

by letting $G'' = G\Delta/\pi$ then

9. Nielsen, L. E., Mechanical Properties of Polymers, Reinhold, New York, (1962).
10. McCrum, N. G., Read, B. E., and Williams, G., Anelastic and Dielectric Effects in Polymeric Solids, John Wiley and Sons p. 122, (1967).

$$\left\langle \frac{1}{H} \right\rangle_{av}^{-1} = \frac{R\pi^2 (G_U - G_R)}{2 \int_0^\infty G \Delta d(1/T)} \quad (\text{cal/mole}) \quad (4)$$

where R is the gas constant ($1.98 \text{ cal/mol-}^\circ\text{K}$). G_U and G_R are the unrelaxed and relaxed values of the shear modulus (dynes/cm^2). The method to determine G_U and G_R is illustrated by Arridge and Speake.¹¹ The integral is determined from the area under the shear modulus (G) times the logarithmic decrement (Δ) curve versus reciprocal temperature ($^\circ\text{K}$).

Arrhenius Shift - The data from the TP were determined at approximately 1 Hz and over a broad temperature range. By applying the Arrhenius shift to the TP data, the data can be shifted to 1.8 MHz and over a broad temperature range between -50 to 250°C . The Arrhenius expression is

$$\ln \frac{f_2}{f_1} = - \frac{\Delta H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad (5)$$

where f_1 is the reference frequency in Hz, and f_2 is the shifted frequency in Hz (1.8 MHz). Values of T_1 in $^\circ\text{K}$ are obtained from the TP data and T_2 also in $^\circ\text{K}$ represents the shifted temperature. The reference frequency was determined to be 1.8 Hz . This reference frequency is the average frequency of the epoxy-diamine polymers in free oscillation in the temperature region of the γ transition.

Shear Sound Speed and Absorption - The shear sound speed (v_s) was calculated from the shear modulus by using the expression

$$v_s = \sqrt{G/\rho} \quad (\text{cm/sec}) \quad (6)$$

where ρ is density (g/cm^3). The absorption (α) was determined from the logarithmic decrement Δ by applying the expression

$$\alpha = 8.686 \Delta \pi f / v_s \quad (\text{dB/cm}). \quad (7)$$

11. Arridge, R. G. C., and Speake, J. H., Polym., 13, 450 (1972).

RESULTS AND DISCUSSION

Torsional Pendulum - The epoxy-diamine polymers have at most three transitions in the temperature range investigated here. The temperatures at which these transitions occurred are determined by the peak maximums on the logarithmic decrement (damping) versus temperature curves (Figures 1, 2, and 3). The transition temperatures are listed in Table 2. In Figure 1 the damping curves for the polymers of RDGE is shown. The glass transition (T_g) is represented by the tallest peak on the damping curve. The glass transition temperature varied with different amine structures. The aromatic amine MPDA gave a higher T_g value (approximately 50 to 70° greater) than the aliphatic amines (Table 1). Among the aliphatic amines the T_g varied within a 22° range. The T_g decreased with increasing length of the aliphatic amine molecule (PDA: 93°C, HDA: 92°C, and DDA: 75°C). These results indicate that the T_g was dependent upon the degree of aromaticity and in the case of aliphatic molecules the T_g was also dependent on the length of the aliphatic molecule. The glass transition has been known to be associated with the crankshaft motion of the polymer backbone,⁹ and if the backbone is stiff and contains bulky pendant groups, then the T_g should increase with decreasing flexibility of the backbone. In this case the amine MPDA is a relative rigid molecule in comparison to PDA, HDA, and DDA. In these aliphatic amines the flexibility comes from the rotation of the methylene groups. If the number of methylene groups increases the crosslink density decreases, the polymer chains are not as rigidly held in the network, then the T_g decreases.

There are two sub-glass transitions. The β transition occurs in the temperature range between 70 and 95°C. As the glass transition temperatures approach the temperature of this β transition, this sub-glass transition becomes progressively less pronounced because the peak of the glass transition overlaps this β peak. The β transition has been associated with the main glass transition of the undercured resin network.¹² The γ transition is broad and is between -60 and -35°C. The transition peaks were distributed over a 3° temperature range. The γ transition has been attributed to the craftshaft type rotation of the segment $-\text{CH}_2\text{CHOHOCH}_2\text{O}-$.¹³

Figure 2 represents the damping curves for the polymers of DGEBA. The glass transition temperature with respect to the diamine decreased for the polymers of DGEBA in a similar manner to the polymers of RDGE (the T_g of MPDA > PDA > HDA > DDA). However the T_g 's of the polymers of DGEBA with similar amines were 28 to 42° greater than the polymers of RDGE (Table 2). For the polymer of DGEBA and MPDA the β transition temperature (95°) was determined from the peak maximum. For the other polymers this temperature was not possible to determine. The β

12. Pogany, G. A., *J. Mat. Sci.* 4, 405 (1969).

13. Schatzki, T. F., *J. Polym. Sci.*, 57, 496 (1962).

transition for the polymers of DGEBA occurs in approximately the same temperatures range as for the polymers of RDGE. The γ transition for the polymers of DGEBA was distributed over a 21° temperature range which was greater than the range found for the polymers of RDGE by a factor of 7.

Figure 3 presents the damping curves for the polymers of BDGE. The trend of the T_g for the polymers of BDGE was affected by the structure of the amines similar to the previous polymers. However the T_g 's of the polymers of BDGE were drastically reduced by as much as 140°C in comparison to the polymers of DGEBA. For the three aliphatic amines the glass transitions were below room temperature (Table 2). This result indicates that the degree of aromaticity of the epoxy also has a dramatic effect on the T_g . The β transition peak was less noticable than the previous polymers of RDGE and DGEBA. The γ transition was not as broad as the previous polymers. The transitions were distributed in a temperature range between -43 and -55, a 12° difference.

The shear modulus versus temperature plots are presented in Figures 4, 5, and 6. In Figure 4 the shear modulus curves for the polymers of RDGE are shown. The shear modulus decreased with increasing temperature. When comparing a portion of the shear modulus curve in the glassy region between -150 and 50°C for the polymers cured with the four diamines, Figure 4 shows that the shear modulus curve for polymers cured with MPDA was greater than polymers cured with PDA, also polymers cured with PDA was greater than HDA as HDA was greater than DDA. However, this trend did not hold true with the other two epoxies. This result suggests that the shear modulus is also dependent on the degree of aromaticity of the amine and, in the case of the aliphatic amines, the length of the methylene chain. Figure 5 contains the shear modulus curves for the polymers of DGEBA. In comparison with the polymers of RDGE the trend of the shear modulus curves of the aliphatic amines was similar, except MPDA was slightly lower than PDA. Figure 6 presents the shear modulus curves for the polymers of BDGE. Comparing with the previous two cases, again the trend was similar for the aliphatic amines, however MPDA was lower than PDA and HDA. From these results the shear modulus curve in the glassy-region of MPDA was not consistently greater than PDA whereas in the aliphatic amines the trend was always as follows: PDA, HDA, and DDA.

Figure 7 represents a trace of the upper and lower limits of the four shear modulus curves of Figures 4, 5, and 6. The upper limit of the polymers of RDGE in the glassy region was greater than the polymers of DGEBA and BDGE. Also the lower limit of the polymers of RDGE was lower than the polymers of DGEBA and BDGE. In the glassy region, the difference between the upper and lower limits for the polymers of DGEBA and BDGE was narrower than the polymers of RDGE. For some engineering applications one would prefer the modulus to be in the glassy region over a large temperature range.

The glassy state of the polymers of DGEBA spans over 300 degrees, while the polymers of RDGE covers 275 degrees and polymers of BDGE 150 degrees. However the modulus of the polymers of DGEBA dropped 0.5 of a decade over the 300 degree range and the polymers of RDGE and BDGE dropped only 0.25 in 275 degrees and 0.2 in 150 degrees of a decade, respectively.

Activation Energies - The activation energies for the γ transition are listed in Table 3. The activation energies for the polymers of BDGE cured with the three aliphatic amines could not be determined because the area under the γ peak could not be separated from the T_g peak (Figure 3). The range of the activation energies was from 17 to 29 kcal/mole. These values of activation energy were in reasonable agreement with values obtained by Arridge and Speake¹¹ and Krehling and Kline¹ who found values that varied from 16 to 25 kcal/mol for the polymer of DGEBA and MPDA.

A plot of activation energy versus glass transition temperature is presented in Figure 8. The numbered data points are from a paper by Boyer.¹⁴ Boyer's data were determined from linear polymers and their glass transition temperatures are low compare to the epoxy-diamine polymers. On the average the activation energies of the epoxy-diamine polymers were greater than the linear polymers. The slope of the line (solid) through Boyer's data was 0.06 cal/mole $^{\circ}\text{K}$. The slope of the data of Boyer and the epoxy-diamine polymers was 0.04 cal/mole $^{\circ}\text{K}$. With the addition of the epoxy-diamine polymers the slope was in fair agreement with Boyer's data.

Shear Sound Speed and Absorption-Plots of shear sound speed versus temperature at 1.8 MHz for the polymers of RDGE, DGEBA, and BDGE are presented in Figures 9, 10, and 13, respectively. In Figure 9 the shear sound speed for the polymers of RDGE decreased as the temperature increased. As the length of the aliphatic chain increased the sound speed also decreased. For example, at 25 $^{\circ}\text{C}$ the sound speed was 8.5×10^4 for PDA, 8.18×10^4 for HDA, and 6.7×10^4 cm/sec for DDA. For the aromatic amine MPDA the sound speed was about the same as PDA at 25 $^{\circ}\text{C}$, 8.5×10^4 cm/sec. The sound speed of MPDA did not drop off with temperature as rapidly as with the aliphatic amine above 150 $^{\circ}\text{C}$. In Figure 10 the sound speed also decreased with temperature for the polymers of DGEBA. At 25 $^{\circ}\text{C}$ the sound speed decreased as follows 8.28×10^4 PDA, 7.82×10^4 : HDA, 7.68×10^4 : DDA, and 7.37×10^4 cm/sec: MPDA. This decreasing trend was expected and was previously observed in the shear modulus versus temperature curves, because the shear sound speed is related to the shear modulus through equation 6. In Figure 13 the sound speed of MPDA with BDGE is more dependant on temperature than with RDGE and DGEBA. The sound speed drops very rapidly with increasing temperature.

14. Boyer, R. G., Rubber Chem. and Techn., 36, 5, 1.

Plots of shear sound absorption versus temperature at 1.8 MHz are presented in Figures 11, 12, and 13 for the polymers of RDGE, DGEBA, and BDGE, respectively. These peaks represent the γ transition that has been shifted to higher temperatures. The temperatures at which the peak maximums occur are listed in Table 2. The peak maximum values follow this trend: DDA > HDA > MPDA > PDA in both RDGE and DGEBA.

CONCLUSIONS AND RECOMMENDATIONS

From the torsional pendulum results the following conclusions were made:

- In these polymers there are at most three transitions in the temperature range of -150 to 200°C.
- The glass transition temperatures for the polymers of DGEBA were 28 to 42° greater than the polymers of RDGE and 140° greater than the polymers of BDGE.
- The glass transition was strongly influenced by the degree of aromaticity and chain length of the monomers.
- The γ transition was found in the temperature range of -57 to -35°C and this transition was not as dependent on the monomer structure as the glass transition.

From the activation energy results the following conclusions were made:

- The activation energies were between 17 and 29 kcal/mole.
- A linear dependence existed between the activation energy and the glass transition temperature, where the slope of the line was 0.04 cal/mole °K, which was in fair agreement with Boyer's data.

From the shear sound speed and absorption results at 1.8 MHz the following conclusions were made.

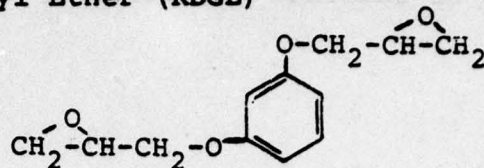
- The shear sound speed decreased with temperature and increasing length of the aliphatic amine molecule.
- The γ transition, which occurs approximately at -55°C at 1 Hz, dominates the ultrasonic properties of these polymers around room temperature.

Further studies, since the ultrasonic properties were predicted here, in the area of ultrasonic measurement are recommended to determine the accuracy of the above predictions. Also since the predictions of the ultrasonic properties relied heavily on the value of the ΔH of the λ transition, other methods, for instance dielectric measurements, should be examined to determine a more accurate ΔH .

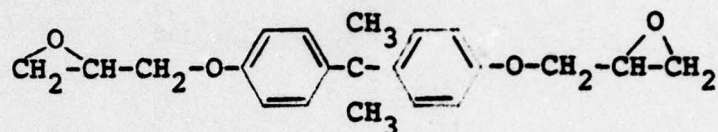
Table 1

Structures of the Epoxy and Amine Monomers

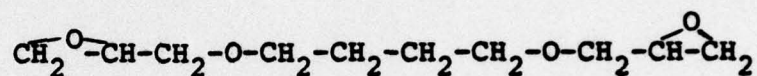
Resorcinol Diglycidyl Ether (RDGE)



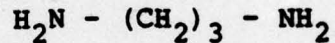
Diglycidyl Ether of Bisphenol A (DGEBA)



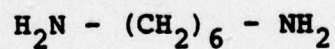
1,4-Butandiol Diglycidyl Ether (BDGE)



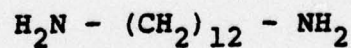
1,3-Propanediamine (PDA)



1,6 - Hexanediamine (HDA)



1,12 - Dodecanediamine (DDA)



m-Phenylenediamine (MPDA)

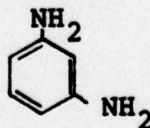


Table 2

Transition Temperatures of Several Epoxy - Amine Polymers

Monomers		Transition Temperatures, °C			
Epoxy	Amines	γ	γ^1	β	T_g
RDGE	PDA	-35	38		93
RDGE	HDA	-37	32.5		92
RDGE	DDA	-38	20		75
RDGE	MPDA	-36	53		146
DGEBA	PDA	-36	57		136
DGEBA	HDA	-36	47.5		115
DGEBA	DDA	-40	38		103
DGEBA	MPDA	-57	52	95	188
BDGE	DDA	-43			8
BDGE	HDA	-53			0
BDGE	DDA	-55			-4
BDGE	MPDA	-55	-8		47

RDGE: Resorcinol Diglycidyl Ether
 DGEBA: Diglycidyl Ether of Bisphenol A
 BDGE: 1,4-Butanediol Diglycidyl Ether
 PDA: 1,3-Propanediamine
 HDA: 1,6-Hexanediamine
 DDA: 1,12-Dodecanediamine
 MPDA: m-Phenylenediamine

1. At 1.8 MHz

Table 3

Activation Energies of Several Epoxy-Amine Polymers

<u>Epoxy</u>	<u>Amine</u>	<u>ΔH, kcal/mole</u>
RDGE	PDA	15
	HDA	24.3
	DDA	29.3
	MPDA	22.3
DGEBA	PDA	25
	HDA	17
	DDA	27.7
	MPDA	19
BDGE	PDA	-
	HDA	-
	DDA	-
	MPDA	19.8

RDGE: Resorcinol Diglycidyl Ether
 DGEBA: Diglycidyl Ether of Bisphenol A
 BDGE: 1,4-Butanediol Diglycidyl Ether
 PDA: 1,3-Propanediamine
 HDA: 1,6-Hexanediamine
 DDA: 1,12-Dodecanediamine
 MPDA: m-Phenylenediamine

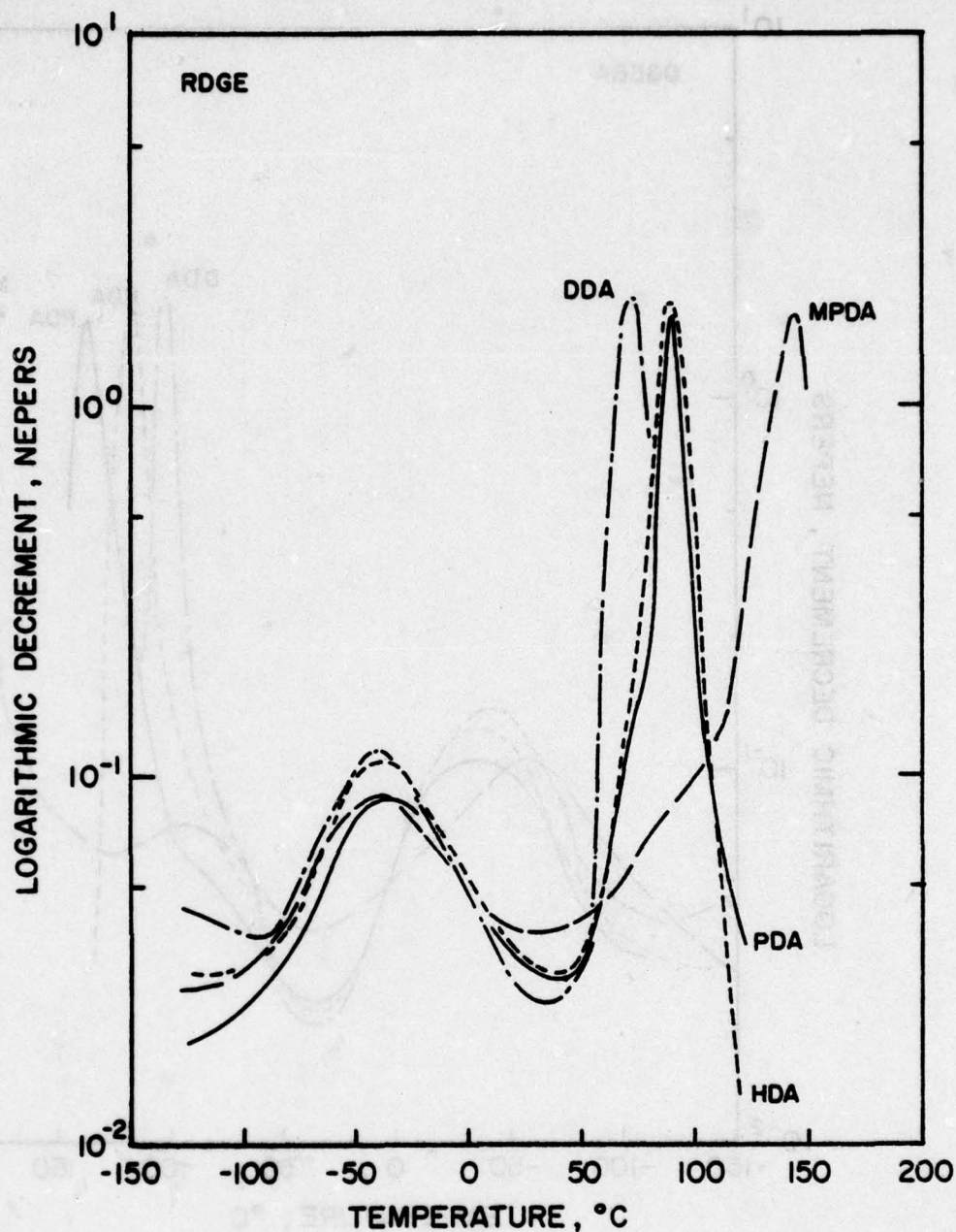


FIG. 1 LOGARITHMIC DECREMENT VERSUS TEMPERATURE OF RESORCINOL DIGLYCIDYL ETHER (RDGE) WITH 1,3-PROPANE-DIAMINE (PDA), 1,6-HEXANEDIAMINE (HDA), 1,12-DODECANEDIAMINE (DDA), AND *m*-PHENYLENEDIAMINE (MPDA)

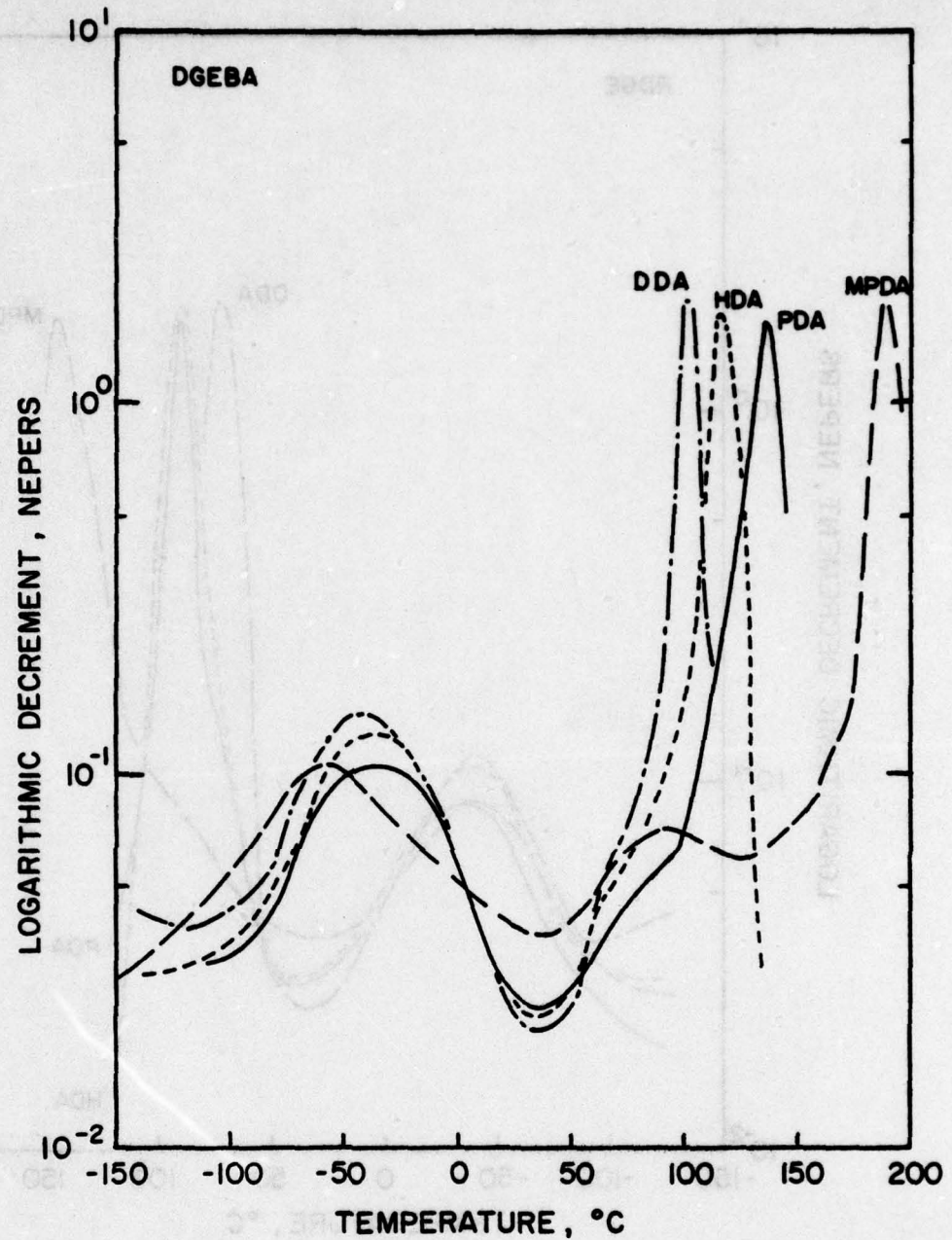


FIG.- 2 LOGARITHMIC DECREMENT VERSUS TEMPERATURE OF DIGLYCIDYL ETHER OF BISPHENOL A (DGEBA) WITH 1,3-PROPANEDIAMINE (PDA), 1,6-HEXANEDIAMINE (HDA), 1,12-DODECANEDIAMINE (DDA), AND m-PHENYLENEDIAMINE (MPDA).

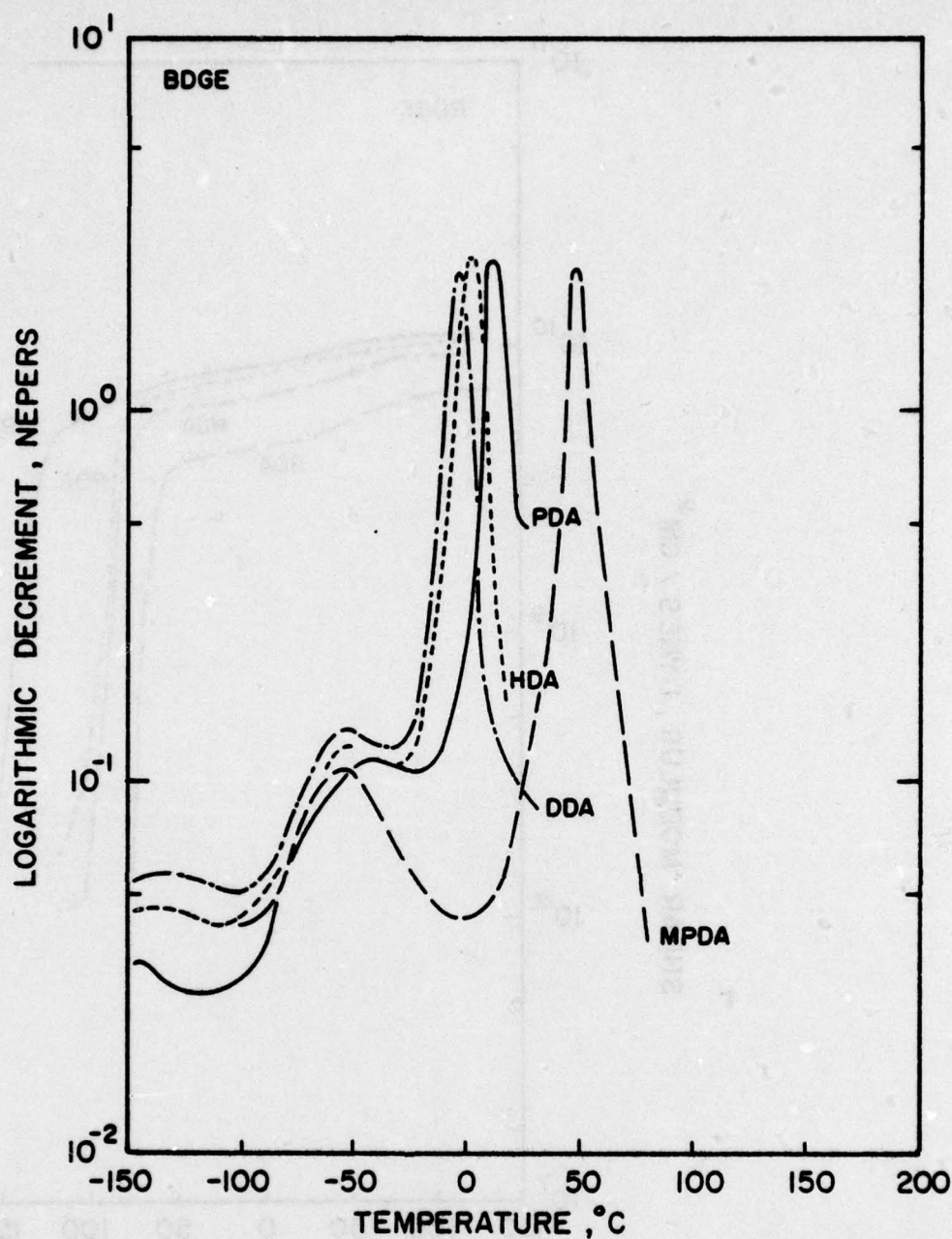


FIG.-3 LOGARITHMIC DECREMENT VERSUS TEMPERATURE OF 1,4-BUTANEDIOL DIGLYCIDYL ETHER (BDGE) WITH 1,3-PROPANE-DIAMINE (PDA), 1,6-HEXANEDIAMINE (HDA), 1,12-DODECANEDIAMINE (DDA), AND *m*-PHENYLENEDIAMINE (MPDA).

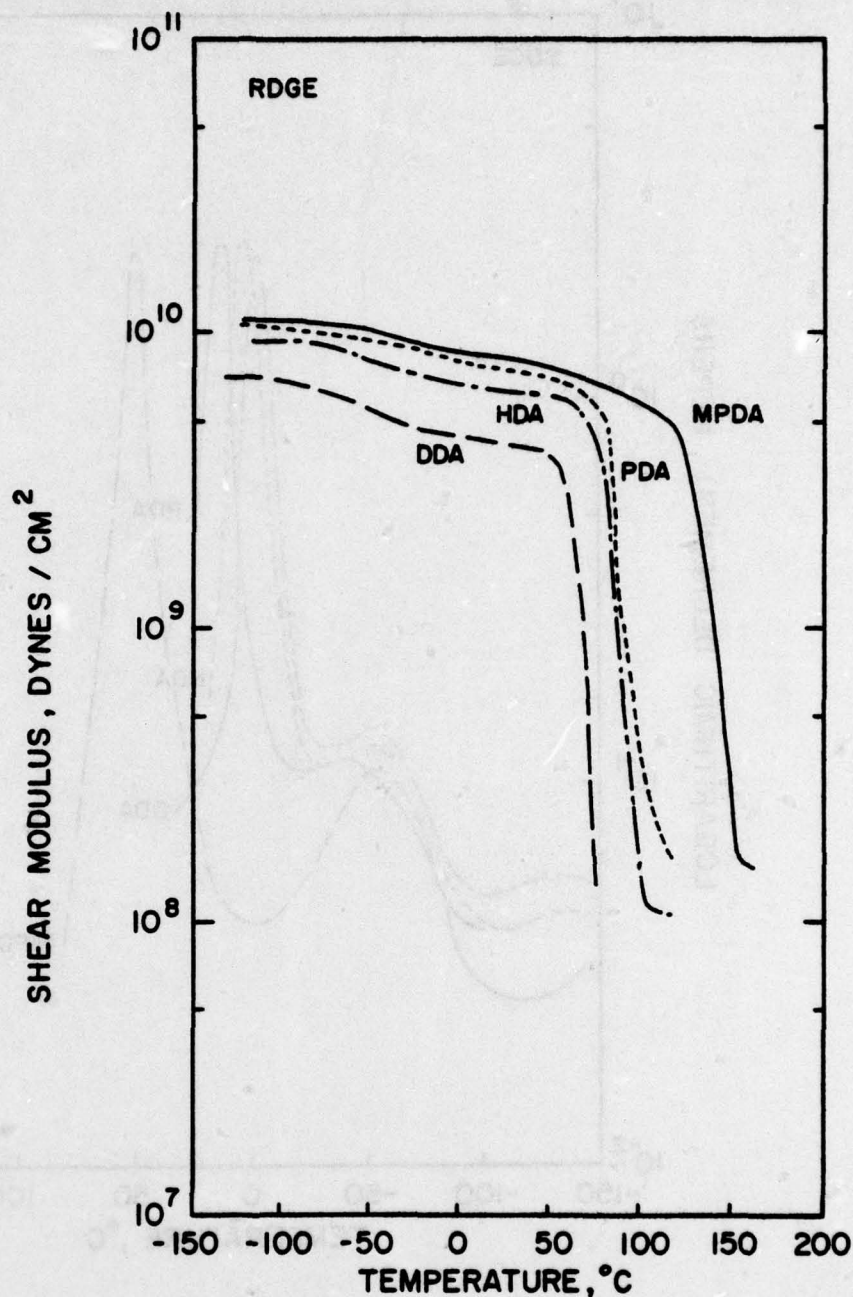


FIG.-4 SHEAR MODULUS VERSUS TEMPERATURE OF RESORCINOL DIGLYCIDYL ETHER (RDGE) WITH 1,3-PROPANEDIAMINE (PDA), 1,6-HEXANEDIAMINE (HDA), 1,12-DODECANEDIAMINE (DDA), AND *m*-PHENYLENEDIAMINE (MPDA).

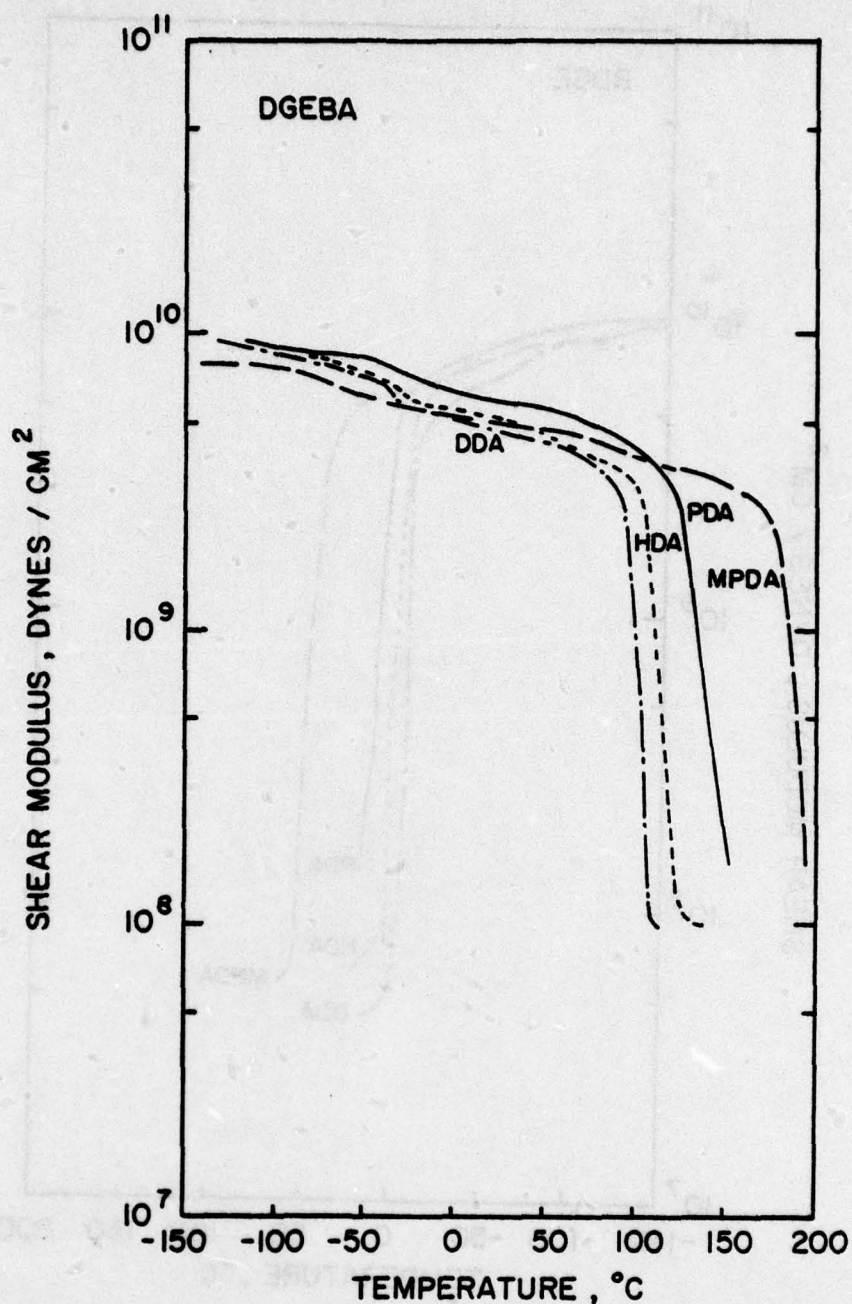


FIG. 5 SHEAR MODULUS VERSUS TEMPERATURE OF DIGLYCIDYL ETHER OF BISPHENOL A (DGEBA) WITH 1,3-PROPANEDIAMINE (PDA), 1,6-HEXANEDIAMINE (HDA), 1,12-DODECANEDIAMINE (DDA), AND *m*-PHENYLENEDIAMINE (MPDA).

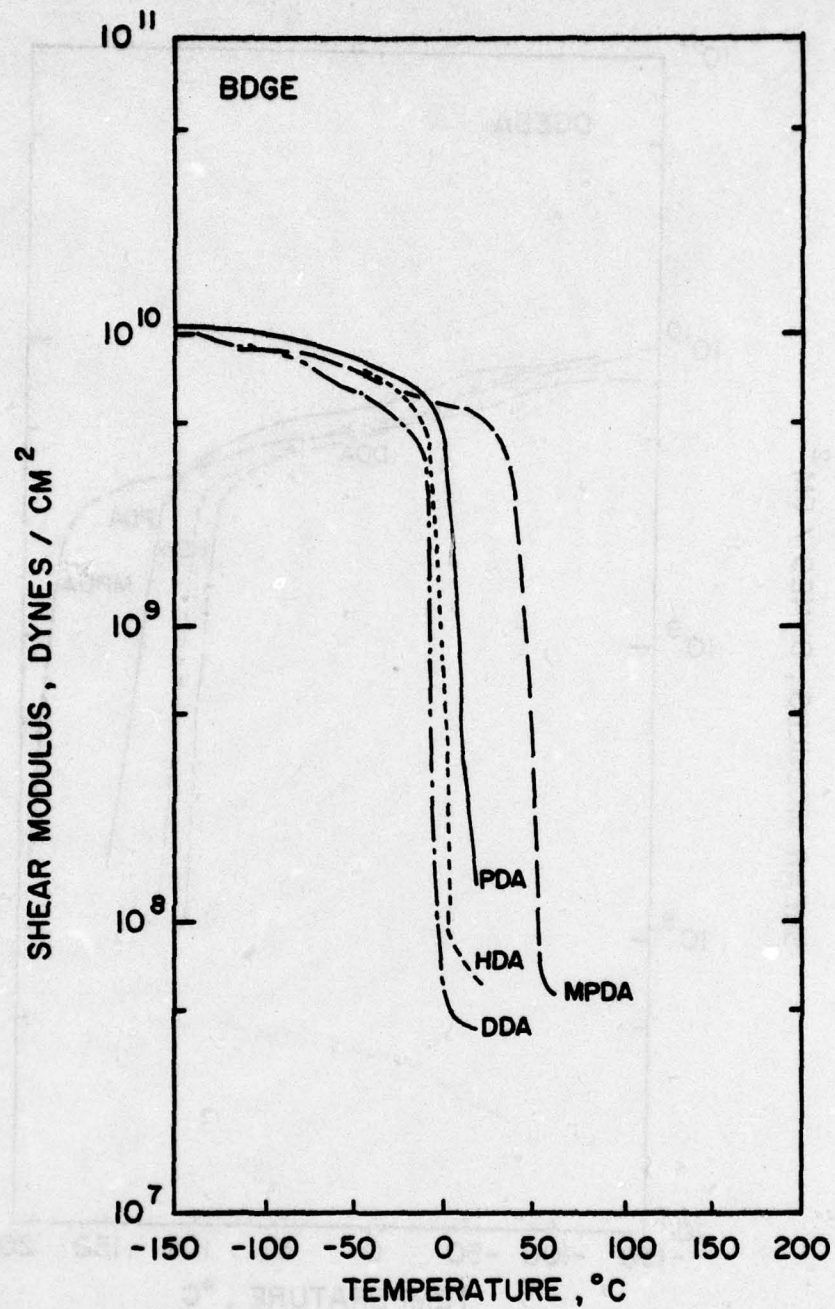


FIG.-6 SHEAR MODULUS VERSUS TEMPERATURE OF 1,4 - BUTANEDIOL DIGLYCIDYL ETHER (BDGE) WITH 1,3-PROPANEDIAMINE (PDA), 1,6 - HEXANEDIAMINE (HDA), 1,12 - DODECANEDIAMINE (DDA), AND *m* - PHENYLENEDIAMINE (MPDA).

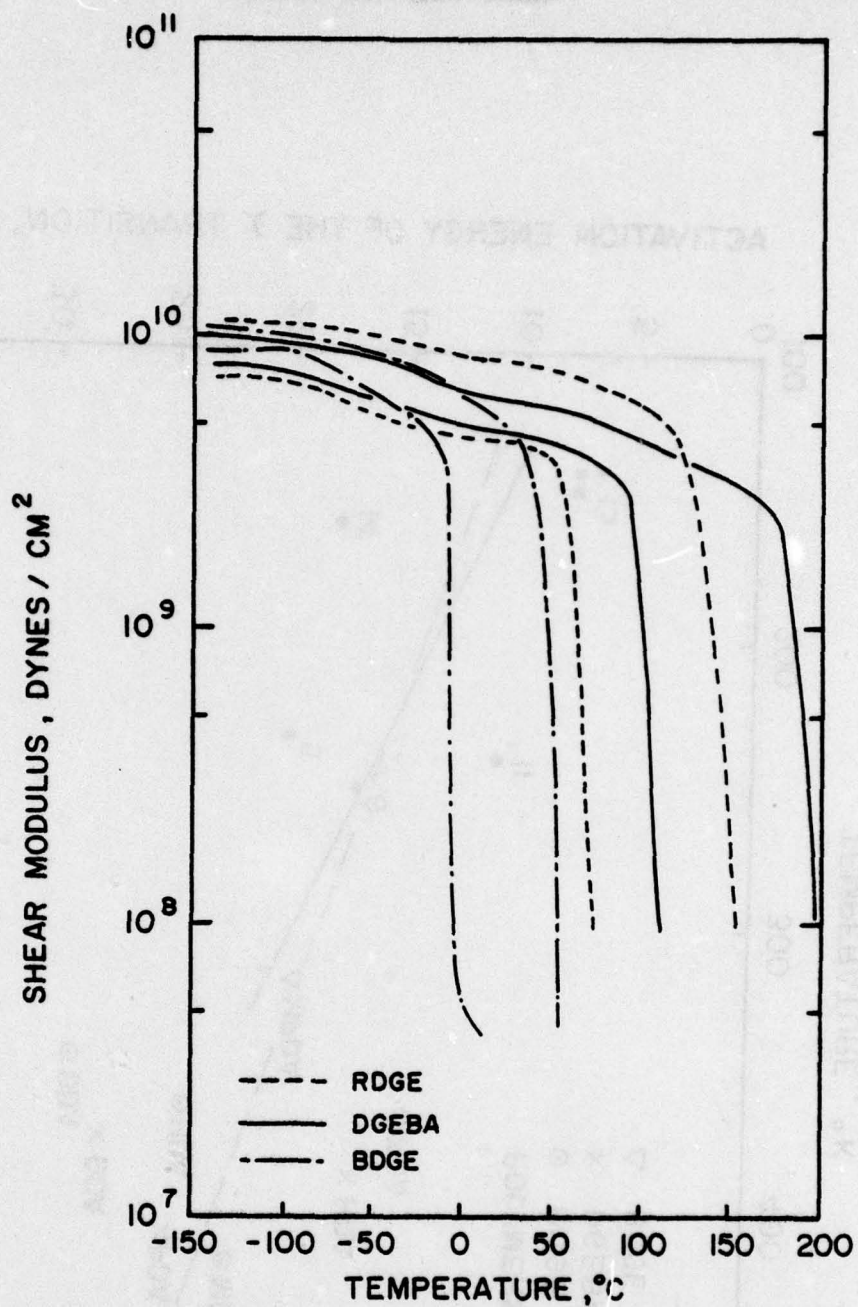
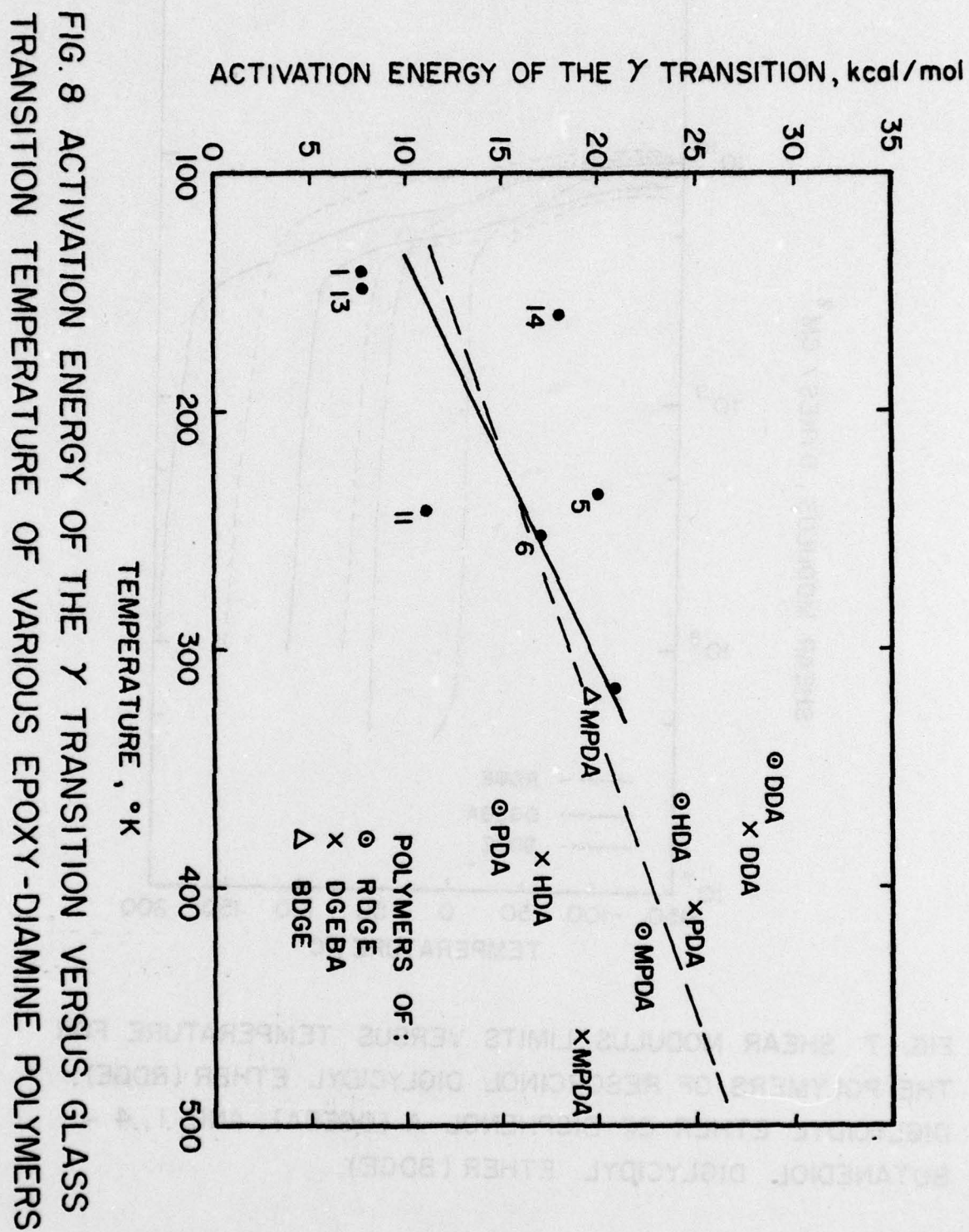


FIG.-7 SHEAR MODULUS LIMITS VERSUS TEMPERATURE FOR THE POLYMERS OF RESORCINOL DIGLYCIDYL ETHER (RDGE), DIGLYCIDYL ETHER OF BISPHENOL A (DGEBA), AND 1, 4 - BUTANEDIOL DIGLYCIDYL ETHER (BDGE).



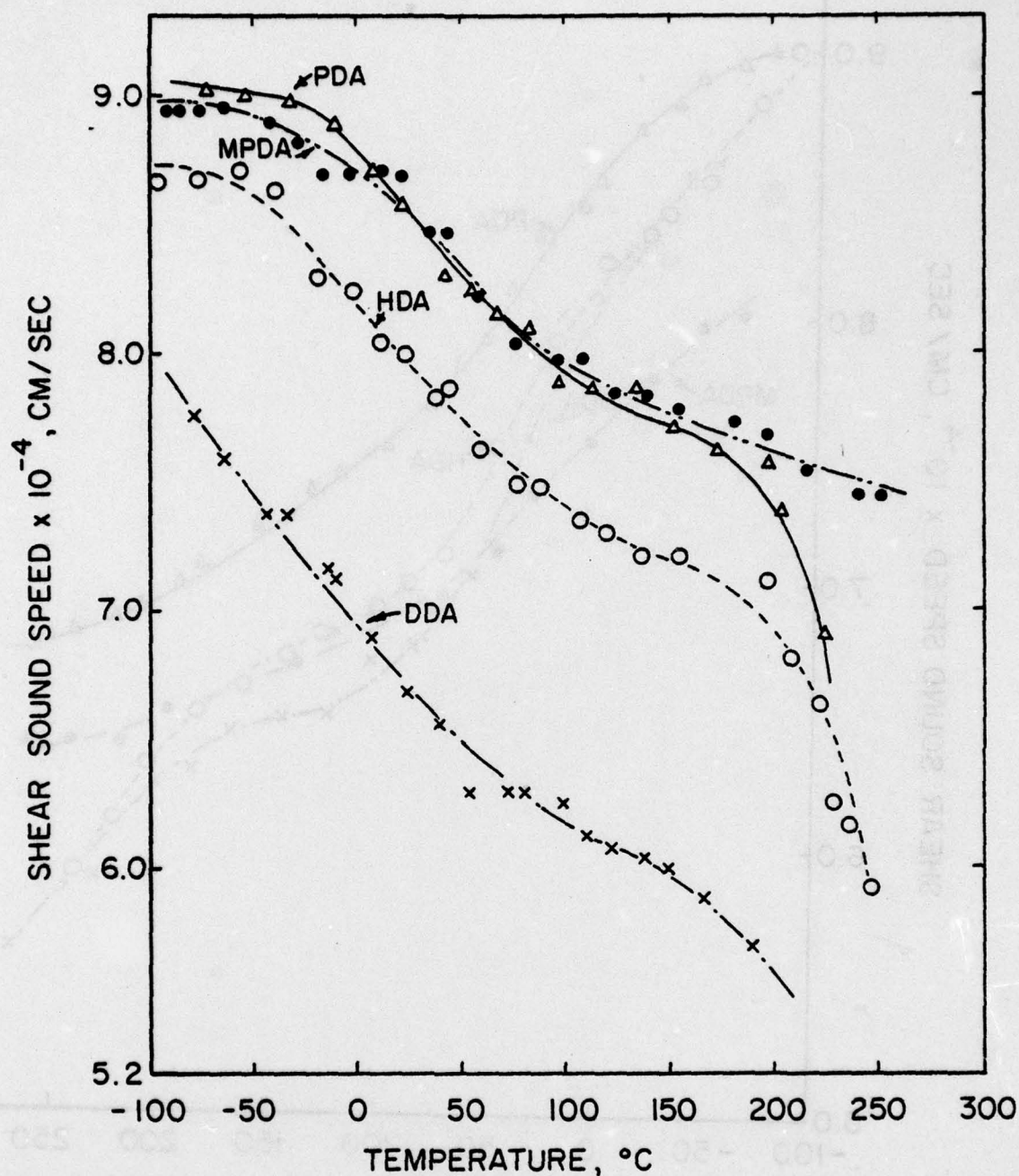


FIG. 9 SHEAR SOUND SPEED VERSUS TEMPERATURE OF THE POLYMERS OF RESORCINOL DIGLYCIDYL ETHER AT 1.8 MHz

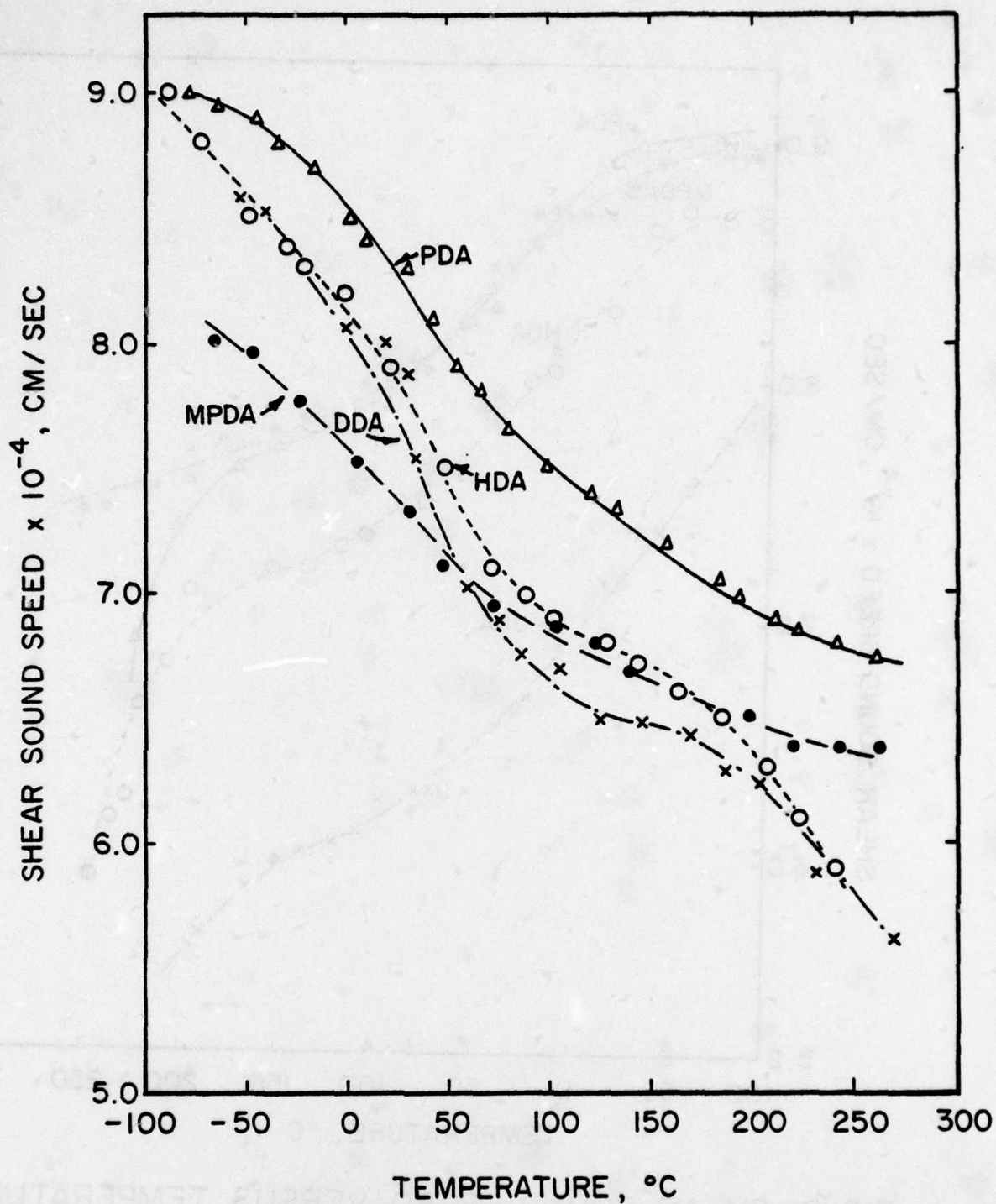


FIG. 10 SHEAR SOUND SPEED VERSUS TEMPERATURE OF THE POLYMERS OF DIGLYCIDYL ETHER OF BISPHENOL A AT 1.8 MHz

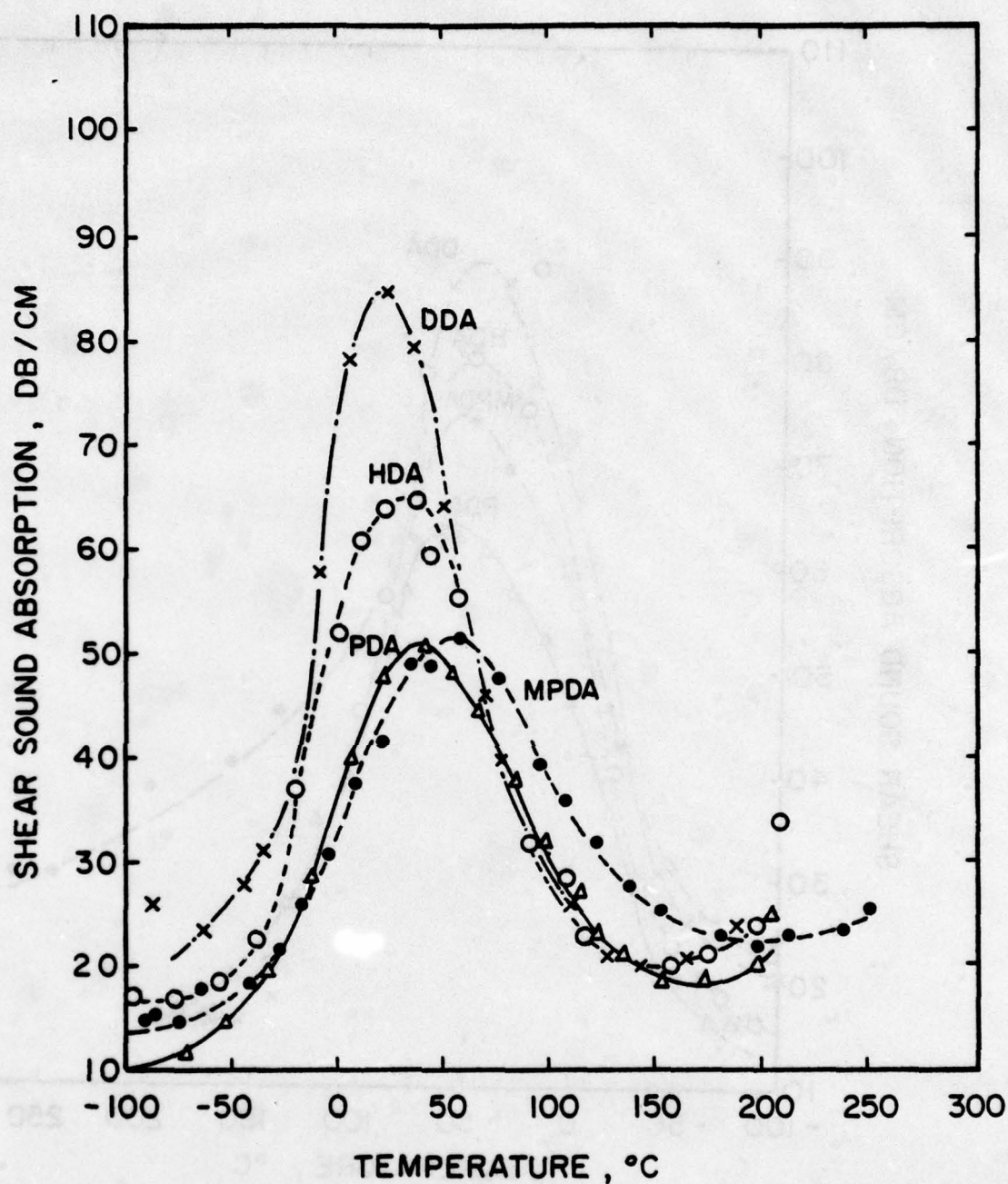


FIG. II SHEAR SOUND ABSORPTION VERSUS TEMPERATURE OF THE POLYMERS OF RESORCINOL DIGLYCIDYL ETHER AT 1.8 MHz

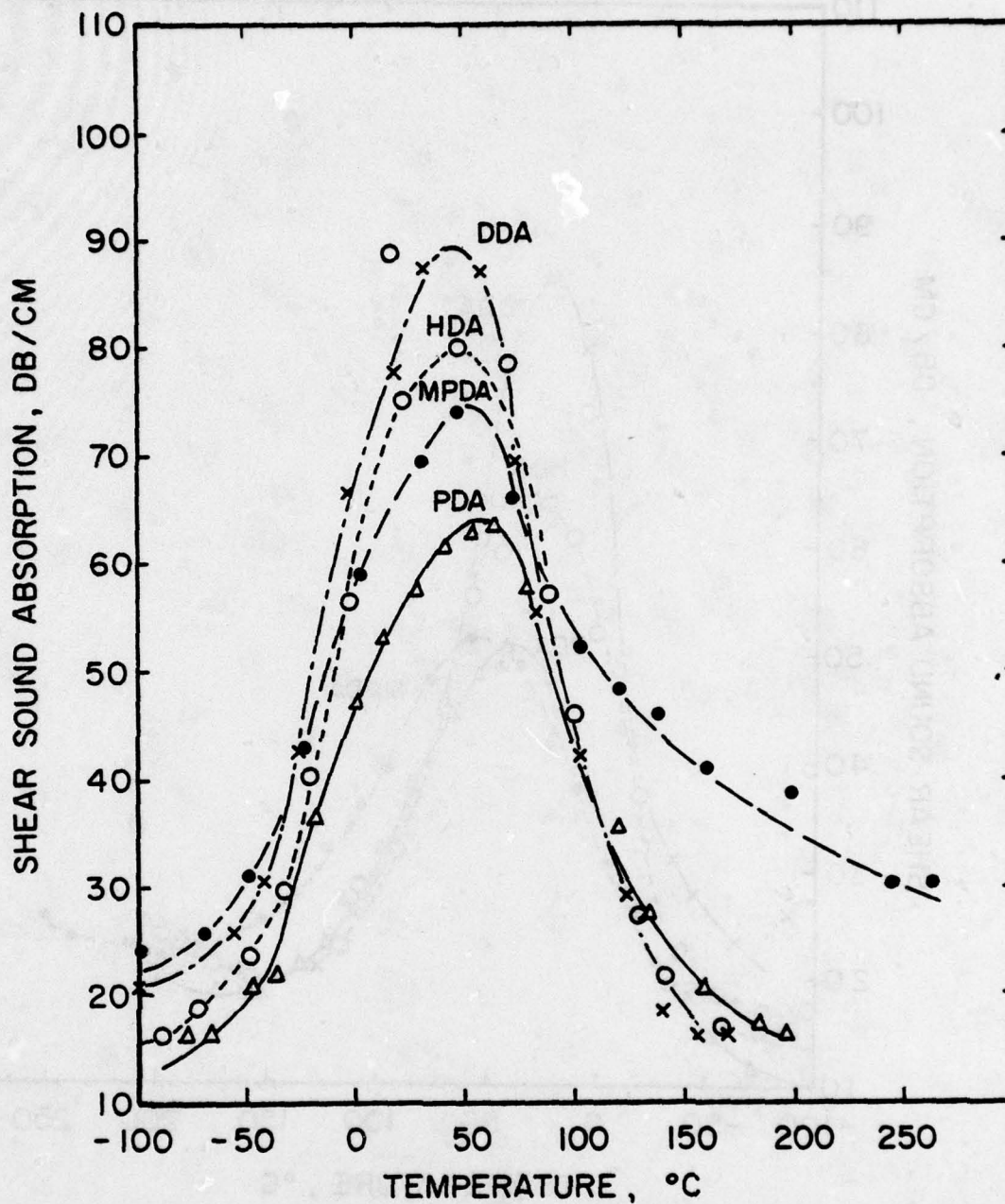


FIG. 12 SHEAR SOUND ABSORPTION VERSUS TEMPERATURE OF THE POLYMER OF DIGLYCIDYL ETHER OF BISPHENOL A AT 1.8 MHz

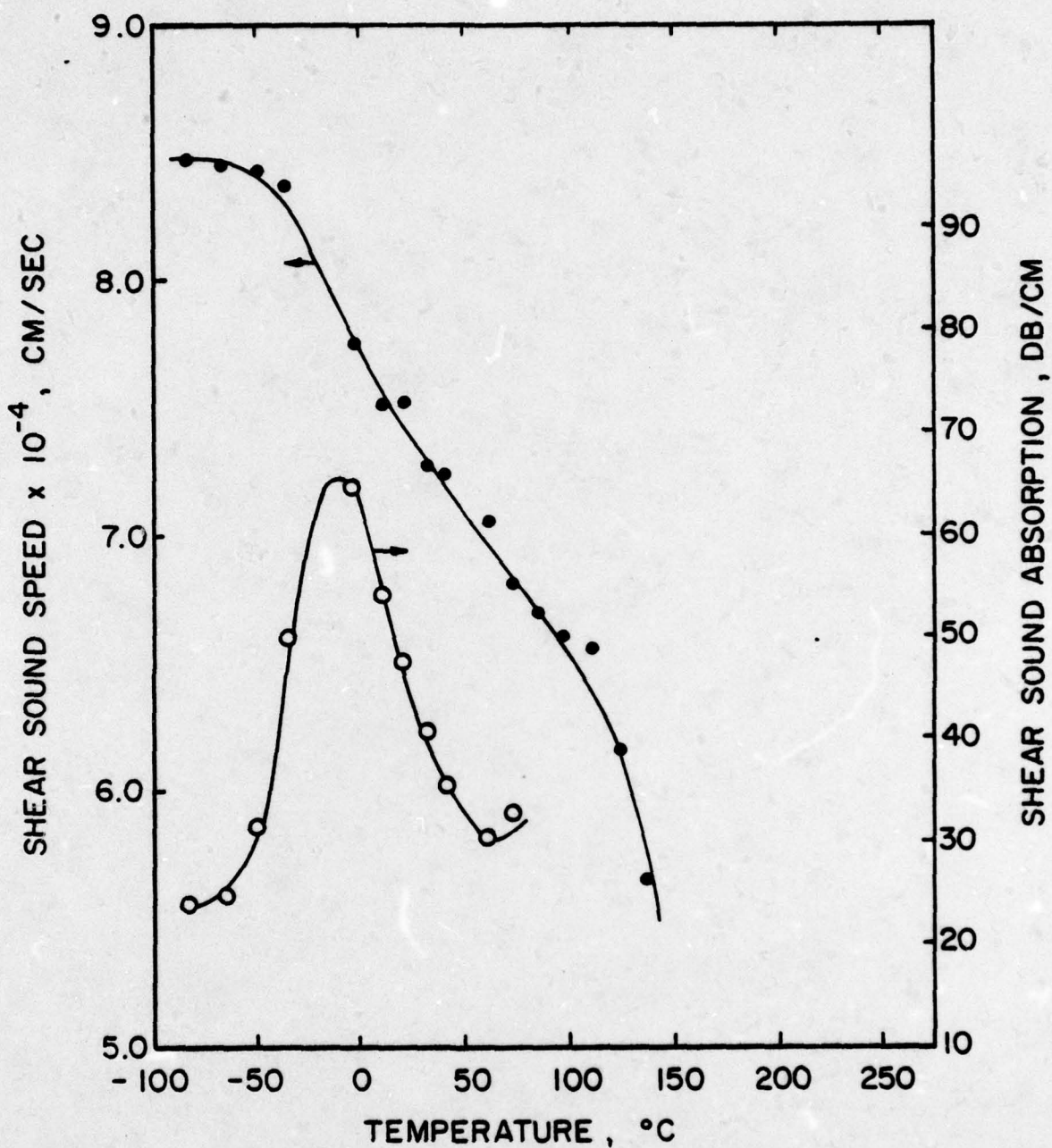


FIG. 13 SHEAR SOUND SPEED AND ABSORPTION OF BUTANEDIOL DIGLYCIDYL ETHER WITH *m*-PHENYLENEDIAMINE

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